

MICROPOROUS SOLID ELECTROLYTES AND
METHODS FOR PREPARING THEM

5 **Technical Field**

10 The present invention relates to an electrolyte film usable in rechargeable cells. More particularly, it relates to a provision of pathways for ions mobile between a cathode and an anode during repeated charge and discharge of rechargeable cells by introducing liquid components and lithium salts (hereinafter, both are referred to as "liquid electrolytes") to an electrolyte film having microporous structures and containing an absorbent.

15 Electrochemical cells include three essential components, i.e., cathode, anode and electrolyte. Examples of materials for said anode are typically compounds in which lithium metal or lithium ions can be intercalated, preferably carbon and polymer materials. Examples of materials for said cathode are typically materials in which lithium ions
20 can be intercalated. For example, oxide compounds or polymer materials such as lithium cobalt oxide (Li_xCoO_2), lithium nickel oxide (Li_xNiO_2), lithium nickel cobalt oxide ($\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$), spinel type lithium manganese oxide ($\text{Li}_x\text{Mn}_2\text{O}_4$) and manganese dioxide (MnO_2) can be used. The introduction of a liquid electrolyte to said electrolyte
25 film can lead to the formation of an ion conductive matrix.

Background Art

Electrochemical cells using polymer electrolytes have some
5 advantages over ones using liquid electrolytes in that i) they have less
leakage risk of liquid; ii) they have excellent electrochemical stability,
which makes it possible to manufacture various types of cells; and iii)
they make the automation of the manufacturing process easy.

10 Since the fact that polymers such as polyoxyethylene may have
metal ionic conductivity in case that they contain polar heterologous
atoms capable of electric interaction with metal ions was found,
research on ion conductive polymers, i.e., polymer electrolytes has
been actively conducted. However, since pure polymers such as
15 polyoxyethylene have very low ionic conductivity of 10^{-8} S/cm or so at
room temperature, they have a demerit in that they should be
approached to the temperature of approximately 100°C in order to
show ionic conductivity of approximately 10^{-4} S/cm applicable to
electrochemical cells. For this reason, the main stream of the research
20 on polymer electrolytes was concentrated on the improvement of
conductivity.

As the fact that the conduction of ion in polymer electrolytes
requires transfer of polymer chains was found, attempts to improve
25 conductivity of ions have been carried out in a direction of increasing
the flexibility of polymer chains. Blonsky *et al* proposed a method for
manufacturing an electrolyte having increased conductivity of 10^{-5}

S/cm by introducing phosphazene linkages to the main chain of the polymers (*J. Am. Chem. Soc.*, 106, 6854 (1984)). However, said electrolyte has lower conductivity and poor mechanical strength.

5 Alternatively, in order to decrease the crystallinity of polymers, various attempts such as modifying the structure of polymers or adding inorganic materials to polymers have been conducted. However, pure polymer electrolytes consisting of polymers and metal salts (not containing liquid electrolytes) still do not exhibit sufficient
10 conductivity.

On the contrary, gel-type electrolytes disclosed in US Patent 5,219,679 contain liquid electrolytes in their polymer backbones, and thus demonstrate conductivity close to that of liquid electrolytes while
15 exhibiting properties of polymers in their mechanical properties, suggesting the possibility of commercialization to rechargeable battery. Namely, the cell of said patent doesn't need a separate activation procedure of adding a liquid electrolyte, but contains some amount of liquid electrolytes which were incorporated during the manufacture of
20 the polymer electrolytes (a mixture of polymer solution and liquid electrolyte was subjected to casting). However, the electrolytes in the US Patent No. 5,219,679 have problems in that they contain polymers such as polyacrylonitrile which are reactive to lithium metal, and thus the reaction products between electrolytes and lithium electrode come
25 to be accumulated during the storage and use period of the cell, resulting in a constant increase in interfacial resistance.

Meanwhile, Scrosati *et al* manufactured gel-type polymer electrolytes using polymethylmethacrylate having low reactivity with lithium metal (*Electrochim. Acta*, 140, 991 (1995)). These electrolytes which use polymethylmethacrylate as a polymer component have little reactivity with the surface of lithium, and thus have a merit in that the resistance increase phenomenon on the surface of electrode during the storage is insignificant. However, they also have demerits in that they have poor mechanical strength and thus the content of the polymers should be increased to accomplish strength sufficient to form a film, which in turn decreases the conductivity down to 10^{-4} S/cm. In addition, since the gel-type electrolytes contain a large amount of liquid components, it is inevitable that the evaporation of the liquid components on the surface of the electrolytes will occur. For this reason, there have been some risks of causing composition changes due to the loss of liquid components during the storage, which leads to the decrease in conductivity. In addition, this method has a demerit of necessitating a dehumidifying atmosphere wherein moisture is removed to the utmost since lithium salts contained in the liquid electrolytes react and decompose with moisture in the air.

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US Patent Nos. 5,296,318 and 5,418,091 proposed a hybrid polymer electrolyte system to compensate for the said problems. This hybrid polymer electrolyte can minimize the moisture effect on the process of manufacturing electrolytes by adding the liquid electrolytes susceptible to the effect of moisture prior to the packaging of battery, while taking advantage of the merits of gel-type polymer electrolytes (the gel-type polymer electrolytes contain a large amount of liquid

electrolytes and thus the conduction of lithium ion proceeds via liquid phase, thereby having similar conductivity to that of liquid electrolytes). However, since the liquid electrolytes are added after electrolyte film is prepared, it is necessary for the inside of the electrolyte film to have
5 sites capable of absorbing liquid components therein or driving force making the liquid component possible to be penetrated thereinto. To this end, dibutyl phthalate is added as a plasticizer in the step of preparing electrolyte film, and after the assembly of cell is complete, the plasticizer is extracted by the use of an organic solvent such as
10 alcohol or ether to form sites for liquid component being absorbed. However, due to the procedure of extracting dibutyl phthalate utilizing a chemical reaction, the methods have fatal demerits that the reproducibility is low, manufacturing yield is reduced, and the automation for mass production is difficult.

15 Accordingly, the present inventors in Korean Patent Application No. 98-57030 tried to solve the above-mentioned problems of said prior art by means of adding an absorbent capable of absorbing liquid electrolytes to a polymer matrix to form a solid electrolyte film, and
20 after the assembly of the battery, introducing a liquid electrolyte to the activation procedure of the battery.

The electrolyte film of the said solid electrolyte consists of an absorbent and a polymer binder under dried condition. The polymer
25 binder has more or less dense structure. In order to show more excellent lithium ionic conductivity by improving the absorption ability

of a liquid electrolyte, the solid electrolyte of which the stereo structure of the electrolyte film is changed is need.

Disclosure of Invention

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Accordingly, the present invention desires to solve the above mentioned problems encountered in the process for the preparation of a solid electrolyte which comprise of adding an absorbent capable of absorbing liquid electrolytes to a polymer matrix to form an electrolyte film, and after the assembly of the battery. Namely, the present invention introduces microporous structures to the polymer matrix while maintaining the mechanical strength of the electrolyte film as it is, which facilitates the absorption of the liquid electrolyte, which in turn improves the lithium ionic conductivity of the solid electrolyte.

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The term "electrolyte film" used in the specification refers to an electrolyte film which is dried condition and does not contain any liquid electrolytes. The term "solid electrolytes" used in the specification means said electrolyte film having ionic conductivity by incorporating liquid electrolytes thereto. Although the solid electrolytes are not in a complete solid state since they contain liquid electrolytes, they are called "solid electrolytes" in order to be distinguished from the liquid electrolytes because the basic backbone of solid electrolytes starts from the electrolyte film at a solid state. In addition, the term "absorbent" used in the specification means materials capable of absorbing liquid electrolytes or of increasing the ability of the solid electrolytes absorbing liquid electrolytes.

The process for assembling batteries refers to binding a cathode and an anode, which are separately prepared, with an interposed electrolyte film in the manner of lamination or pressing. When the electrolyte film is prepared by one of the said methods, liquid electrolytes are added after the assembly of battery, which can minimize the restriction on dehumidifying conditions in the process. Furthermore, according to the present method, the sites capable of absorbing liquid electrolytes are already formed in the course of manufacturing the electrolyte film and thus there is no need for the procedure of extracting a plasticizer. Therefore, the method has some advantages in that it simplifies the process, which not only reduces the production cost but also makes the automation process easy and improves the yield. In addition, when the electrolyte film is prepared by one of the said methods, the polymer matrix comes to have microporous structures, which facilitates the transfer of the liquid electrolyte, which in turn improves the lithium ionic conductivity of the solid electrolyte with the same amount of absorbent.

20 The solid electrolytes according to the present invention comprise an electrolyte film containing an inorganic absorbent and consisting of microporous structures, and an ion conductive liquid electrolyte.

25 Said electrolyte film can be preferably prepared by means of a phase inversion method. Examples of such method include wet process

and dry process. The wet process refers to a process for the preparation of an electrolyte film, which comprises the steps of:

dissolving a mixture of an absorbent and a polymer binder in a solvent for the polymer binder,

5 making the resulting solution to a film form,

exchanging the solvent with a non-solvent for the polymer binder, and then

drying the resulting material to form an electrolyte film.

10 On the contrary, the dry process refers to a process for the preparation of an electrolyte film, which comprises the steps of:

mixing a mixture of an absorbent and a polymer binder with a solvent for dissolving the polymer binder, a non-solvent which does not dissolve the polymer binder, a pore former and a wetting agent,

15 making the resulting mixture into a film form, and

drying the resulting film completely.

Subsequently, an activation procedure of absorbing an ion conductive liquid electrolyte into thus prepared porous electrolyte film
20 may lead to the formation of a solid electrolyte for rechargeable cells.

Accordingly, the solid electrolyte of the present invention can be prepared by introducing an absorbent capable of absorbing the liquid electrolyte or increasing the absorption ability to the inside of the
25 electrolyte film to form a porous electrolyte film matrix and then injecting an liquid electrolyte thereto. Thus prepared solid electrolyte

has lithium ionic conductivity of approximately $1 \text{ to } 3 \times 10^{-3} \text{ S/cm}$ at room temperature.

Examples of absorbents capable of absorbing liquid electrolytes
5 or increasing the absorption ability include organic materials such as porous polymers and inorganic materials such as mineral particles.

As porous polymer absorbents, polypropylene, polyethylene, polystyrene and polyurethane to which porosity is introduced by means
10 of net type polymer wherein bulky functional groups are introduced to branched chains or by means of adjusting the parameters of the process according to the present invention can be used. Natural polymers such as wood powder, pulp, cellulose and cork may also be used.

As inorganic absorbents, it is possible to use one or two or more
15 particles selected from the group consisting of mineral particles, synthetic oxide compounds particles and mesoporous molecular sieves. Examples of said mineral particles include mineral particles having phyllosilicate structures such as clay, paragonite, montmorillonite and
20 mica. Examples of said synthetic oxide compounds particles include zeolite, porous silica and porous alumina. Examples of mesoporous molecular sieves include mesoporous molecular sieves made of oxide compounds such as silica/polymer substance and having a pore diameter in 2 to 30 nm. Said mineral particles, synthetic oxide
25 compounds particles and mesoporous molecular sieves may be used in the form of a mixture wherein two or more absorbents selected from the above mentioned absorbents are combined.

Said inorganic absorbents have better mechanical, thermal and electrochemical stability as compared to organic absorbents such as porous polymers, and thus the performance properties of the rechargeable cells utilizing inorganic absorbents are better than those of the rechargeable cells utilizing organic absorbents.

Namely, it was found that when cells are fabricated by assembling an anode and a cathode by means of pressing method or lamination method, the organic absorbents differ from the electrolyte films or polymer binders of composite electrodes in their mechanical and thermal behaviors, and thus the rechargeable cells utilizing these organic absorbents show significant reduction in their discharge capacity during repeated charge and discharge as compared to the rechargeable cells utilizing inorganic absorbents. For example, absorbents consisting of organic materials such as polymers with low melting points or deteriorating mechanical strength may lose their absorption ability in the course of pressing or lamination procedures. In other words, the use of organic absorbents such as polymers may be beneficial to the performance of electrolyte films or solid electrolytes themselves, but it may be very difficult to maintain their original performance when cells are fabricated by means of the pressing or lamination method.

In addition, as explained above, since the transfer of polymer chains directly affects the ionic conductivity in general polymer electrolytes, the effect of temperature on ionic conductivity becomes

significant. Particularly, at low temperatures, the transfer of polymer chains is weakened, which significantly reduces the ionic conductivity, thereby resulting in severe deterioration in the performance of the cells. However, the use of absorbents as in the present invention increases the ionic conductivity. Moreover, if a large amount of inorganic absorbent, which is less affected by temperature, is used, the effect of temperature becomes less unlike the properties of general polymer electrolytes. As a large amount of inorganic absorbent is contained in electrolytes, the electrolytes have some merits in that the resistance against ignition or explosion is improved as compared to the electrolytes containing a large amount of organic material such as polymers.

Accordingly, it can be confirmed that it is preferable to use inorganic absorbents rather than use organic absorbents in the constitution of the electrolyte film of rechargeable cells.

The amount of absorbents added is 30 to 95 % by weight and preferably, 50 to 90 % by weight based on the weight of the dried state electrolyte film which does not contain liquid electrolyte. If the added amount exceeds 95 % by weight, the mechanical strength of the electrolyte film formed falls. If the amount is not more than 30 % by weight, the ability to absorb liquid electrolyte decreases.

The particle size of absorbents is preferably not more than 40 μm , more preferably, not more than 20 μm so as not to decrease the mechanical strength and the uniformity of the electrolyte film.

As polymer binders, it is possible to use most common polymers. Among them, it is preferred to use a mixture of one or two or more polymers selected from the group consisting of copolymers of polyvinylidene fluoride, vinylidene fluoride and hexafluoropropylene, 5 copolymers of vinylidene fluoride and maleic anhydride, polyvinylchloride, polymethylmethacrylate, polymethacrylate, cellulose triacetate, polyurethane, polysulfone, polyether, polyolefine such as polyethylene or polypropylene, polyethylene oxide, polyisobutylene, polybutyldiene, polyvinylalcohol, polyacrylonitrile, 10 polyimide, polyvinyl formal, acrylonitrilebutyldiene rubber, ethylene-propylene-diene-monomer, tetra(ethylene glycol)diacrylate, polydimethylsiloxane, polycarbonate and polysilicon, or copolymers thereof.

15 The present invention introduces porous structures to the electrolyte film used as a matrix for the solid electrolyte, which facilitates the transfer of liquid electrolyte, and thus improves the lithium ionic conductivity of the solid electrolyte with the use of same amount of absorbent. As methods for preparing said porous electrolyte 20 film include the wet process and dry process, as explained above. The wet process is carried out by subjecting electrolyte film component to a casting and reacting the resulting film with a non-solvent to form microporous structures in the polymer matrix. The dry process is carried out by subjecting the electrolyte film components together with 25 a non-solvent for introducing porosity and a pore former to molding to form a microporous electrolyte film.

As solvents for dissolving polymer binders, a mixture of one or two or more solvents selected from the group consisting of N-methylpyrrolidinone, dimethylformamide, dimethylacetamide, tetrahydrofuran, acetonitrile, cyclohexanone, chloroform, dichloromethane, hexamethylphosphoramide, dimethylsulfoxide, acetone and dioxane.

As non-solvents for the polymer binder, it is possible to use a mixture of one or two or more selected from the group consisting of water, ethanol, ethylene glycol, glycerol, acetone, dichloromethane, ethylacetate, butanol, pentanol, hexanol and ether.

As pore formers, it is preferred to use a mixture of one or two or more selected from the group consisting of 2-propanol, resorcinol, trifluoroethanol, cyclohexanol, hexafluoroisopropanol, methanol and hemiacetal obtained by the reaction of maleic acid with hexafluoroacetone.

As dipping agents, it is preferred to use nonionic surfactants, for example, Triton X-100 (manufactured by Aldrich Company), Igepal DM-710 (manufactured by GAF Company).

The liquid electrolytes, which contain absorbents and are to be absorbed in electrolyte film, can be prepared by dissolving lithium salt in an organic solvent. In the present invention, the absorption of the liquid electrolytes into electrolyte film is defined as "activation".

It is preferred that said organic solvents have high polarity and no reactivity to lithium metal so as to improve the degree of dissociation of ions by raising the polarity of electrolyte and to facilitate ion conduction by lowering local viscosity around ions.

5 Examples of such organic solvents include ethylene carbonate, propylene carbonate, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, γ -butyrolactone, dimethylsulfoxide, 1,3-dioxane, tetrahydrofuran, 2-methyltetrahydrofuran, sulfolane, N,N-dimethylformamide, diglyme, triglyme and tetraglyme. In particular, it

10 is preferred that the organic solvent is used in the form of mixed solutions of two or more solvents consisting of high viscosity solvents and low viscosity solvents.

Said lithium salt is preferred to have low lattice energy and a

15 high degree of dissociation. Examples of such lithium salt include LiClO_4 , LiBF_4 , LiPF_6 , LiAsF_6 , LiSCN , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and $\text{LiC}(\text{CF}_3\text{SO}_2)_3$. The selective mixtures thereof can also be used. The concentration of the lithium salt is preferably 0.5M to 2M.

20 The liquid electrolyte can be added in an amount of 30 to 90 % by weight, preferably 40 to 85 % by weight, based on the total amount of electrolytes including the liquid electrolyte.

The solid electrolyte according to the present invention is

25 characterized by the facts that it is easy to prepare when compared to prior polymer electrolytes; that it has higher ionic conductivity because the conduction of lithium ions proceeds via liquid phase; and that it is

not affected by moisture or temperature until it absorbs the liquid electrolyte or it is activated.

In the following, the process for the preparation of said solid electrolyte having porous structures is explained in greater detail.

Wet process

The solid electrolyte having porous structures according to the present invention can be prepared by five steps, i.e., mixing an absorbent with a polymer binder, dissolution of the resulting mixture, molding, making polymer matrix porous and drying/ activation.

First of all, an absorbent in powder form (particle size of not more than 40 μm) and a polymer binder are dry mixed in a closed container.

The resulting mixture of the absorbent and the polymer binder is dissolved in a solvent for the polymer binder. The solid content of said mixed solution is preferably 5 to 50 % by weight based on the total weight of the solution. If the content is not more than 5 % by weight, the mechanical strength of the electrolyte film decreases and if the content is more than 50 % by weight, the polymer binder cannot be dissolved sufficiently or the viscosity of the mixed solution becomes large, which is problematic.

In order to facilitate the dissolution of the polymer binder and to avoid the agglomeration between absorbent, a magnetic stirrer, a

mechanical stirrer, a planetary mixer or a high-speed disperser can be used to stir the mixed solution. While stirring, an ultrasonic stirrer may be adopted to prevent the absorbent from agglomerating or bubbling in the middle of mixing. In addition, if desired, the mixed solution may
5 be subjected to defoaming and filtration steps.

After the polymer binder is completely dissolved and uniformly mixed with the absorbent, the resulting mixture is made in the form of film with a regular thickness. For example, the mixed solution may be
10 poured on a flat glass plate or a Teflon plate and then be subjected to casting so that the resulting products have a regular thickness. Alternatively, the mixed solution may be extracted from a die with a regular space and then coated onto a substrate made of polymer film. Various other application methods can be selected. It is preferred that
15 the thickness of the film is controlled in the range of 10 to 200 μm . If the thickness of the film is not more than 10 μm , the mechanical strength decreases, and if the thickness of the film exceeds 200 μm , the ionic conductivity decreases, which is not preferable.

20 After casting in the form of film, in order to introduce porosity to the polymer matrix, the film was contacted with a non-solvent for the polymer binder to extract the solvent for the polymer binder. For example, it is possible to extract the solvent by soaking the film in a non-solvent pool containing a non-solvent. Accordingly, it is preferable
25 to combine a miscible solvent and a non-solvent. The time for soaking the film in a non-solvent pool varies from one minute to one hour depending on the kinds of the solvents and non-solvents. If the time is

shorter than the defined time, it is difficult to obtain sufficient porosity. On the contrary, if the time exceeds the defined time, the productivity becomes decreased, which is not preferable. The temperature in the pool is preferably from 10°C to 90°C, more preferably from 20°C to 80°C. If the temperature is lower than that, it is difficult to obtain sufficient porosity. If the temperature is excessively high, the mechanical strength of the electrolyte film decreases, which is not preferable. In general, it is preferable to introduce porosity corresponding to the amount of solvents in a mixed solution consisting of an absorbent, a polymer binder and a solvent. It is also preferable to control the composition, temperature and time of the mixed solution so that porosity can be introduced in accordance with the amount of solvents in a mixed solution.

After the extraction of the solvent and completely drying the resulting film, the liquid electrolyte is introduced thereto.

Dry process

The solid electrolyte having porous structures according to the present invention can be prepared by dry process consisting of four steps, i.e., mixing an absorbent with a polymer binder, adding additives (solvent, non-solvent, pore former, dipping agent), casting and drying/activation.

An absorbent in powder form (particle size of not more than 40 μm) and a polymer binder are dry mixed in a closed container. The

resulting mixture of absorbent and the polymer binder is dissolved in a solvent for the polymer binder.

5 In order to facilitate the dissolution of the polymer binder and to avoid the agglomeration between absorbent, a magnetic stirrer, a mechanical stirrer, a planetary mixer or a high-speed disperser can be used to stir the mixed solution. While stirring, an ultrasonic stirrer may be used to prevent the absorbent from agglomerating or foaming in the middle of mixing. In addition, if desired, the mixed solution may be
10 subjected to defoaming and filtration steps.

After the polymer binder is completely dissolved and uniformly mixed with the absorbent, a solvent which does not dissolve the polymer binder, i.e., a non-solvent is added in an amount range of not
15 causing the precipitation of the polymer binder. In order to facilitate the formation of microporous structures, it is preferable to add pore formers or dipping agents. After said additives are uniformly mixed, the resulting mixture is molded in the form of film with a regular thickness. For example, the mixed solution may be poured on a flat
20 glass plate or a Teflon plate and then be subjected to casting so that the resulting products have a regular thickness. Alternatively, the mixed solution may be extracted from a die with a regular space and then coated onto a substrate made of polymer film. Besides, various other application methods can be selected. It is preferred that the thickness of
25 the film is controlled in the range of 10 to 200 μm . If the thickness of the film is not more than 10 μm , the mechanical strength decreases, and

if the thickness of the film exceeds 200 μm , the ionic conductivity decreases, which is not preferable.

After the completion of making in the form of film, the resulting
5 electrolyte film is completely dried at 20°C to 200°C and then the liquid electrolyte is introduced thereto.

When compared to the wet process, the dry process has a demerit in that the dispersion or mixing of the absorbents, polymer binders and additives is comparatively difficult. When a complete dispersion or mixing is not conducted, (i) it become difficult to accomplish an even dispersion of pores or absorbents, (ii) it is not easy to cast into the form of an electrolyte film and (iii) the mechanical strength and reproducibility become decrease. Namely, in the event that the pores or absorbents are dispersed unevenly, it was confirmed that (i) the reaction in cells proceeds non-uniformly localized state when the electrolyte film is used as an electrolyte for electrochemical cells; (ii) the casting in the form of film becomes difficult; and (iii) the mechanical strength decreases, which limited the dry process severely.

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In addition, the dry process necessitates the addition of non-solvents in order to form pores and in view of the principle of the dry process, the solvent should be evaporated (dried) prior to the non-solvents so that pores can be formed. If the non-solvents are evaporated prior to the solvents, pores cannot be formed. In this regard, it is essential that the non-solvents should have non-volatile property or higher boiling points than solvents. For this reason, the dry process is

likely to have a problem of residual non-solvents. In other words, non-solvents, which have higher boiling point than solvents or are non-volatile, are difficult to remove completely from the electrolyte film during drying procedure. Therefore, a separate measure (for example,
5 extraction with alcohol or ether or increasing the drying temperature sufficiently) should be taken in order to remove completely the non-solvents. In addition, since said non-solvents are chemically and electrochemically unstable, if said non-solvents remain in the electrolyte film, they may cause side reactions or oxidation or reduction
10 with repeated charge and discharge of cells. As a result, the deterioration of cell performance such as capacity decrease of cells or gas evolution may happen. The same problems apply to the other additives besides non-solvents. It is considered that the process for the preparation of electrolyte film solely consisting of an absorbent and a
15 polymer binder by way of complete removal of additives or the like may be complicated, which render the reproducibility of this process difficult.

Accordingly, it is preferable to prepare the electrolyte films or
20 solid electrolytes by wet process rather than dry process.

The present invention is directed to rechargeable cells, particularly to rechargeable lithium cells wherein said porous solid electrolyte is used as an electrolyte.

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The process for assembling batteries refers to binding a cathode and an anode, which are separately prepared, with an interposed

electrolyte film in the manner of lamination, pressing or winding. When the electrolyte film is prepared by one of the said methods, liquid electrolytes are added after the assembly of battery, which can minimize the restriction on dehumidifying atmosphere in the process.

5 Furthermore, according to the present method, the sites capable of absorbing liquid electrolytes are already formed in the course of manufacturing the electrolyte film and thus there is no need for the procedure of extracting a plasticizer. Therefore, the method has some advantages in that it simplifies the process, which not only reduces the
10 production cost but also makes the automation process easy and improves the yield. In addition, when an electrolyte film is prepared by the said method, the polymer matrix comes to have microporous structures, which facilitates the transfer of the liquid electrolyte and improves the lithium ionic conductivity of the solid electrolyte with the
15 same amount of absorbent.

In one embodiment of the method for the production of rechargeable cells by the use of the solid electrolyte according to the present invention, a cell can be constructed by bonding a cathode and
20 an anode, interposed with the porous electrolyte film prepared from the above-mentioned procedure. The porous electrolyte film contains absorbent powder therein and has porous structures, which make the electrolyte film maintain its condition facilitating the absorption of the liquid electrolyte. The cathode is electrically connected to a cathode
25 current collector; and the anode is electrically connected to an anode current collector. Thus the constructed assembly is activated to be able

to absorb the liquid electrolyte, thereby obtaining an electrochemical cell which is ready to operate.

Fig. 1 illustrates a cross sectional view of the rechargeable cell in which the solid electrolyte according to the present invention is used. The solid electrolyte (1) contains the absorbent powder (11) and the liquid electrolyte, which is absorbed during the activation step. The cathode (2) is electrically connected to a cathode current collector (22) and the anode (3) is electrically connected to an anode current collector (33), respectively.

The procedures for the preparation of the cathode or anode are as follows. The cathode or anode consists of a current collector and an active material layer. The active material layer comprises of active materials, conducting materials and binders, etc. Besides, various additives may be introduced in order to improve the performance of cells. The current collectors, conducting materials, binders and additives, which are contained in the cathode or anode, may be identical or different, depending on desired objectives.

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The current collectors provide mobile pathways for electrons, which are generated in the oxidation/reduction reaction, taking place in the cathode or the anode. As current collectors, generally grids, foils, punching foils and etching foils, etc., may be used, depending on the performance or manufacturing processes of the cell. The use of grids can increase the filling rate of the active material, but it may complicate the manufacturing process. The use of foils can improve the

performance of the cell and simplify the manufacturing process, but it may deteriorate the compactness of the active materials. Copper, aluminum, nickel, titanium, stainless steel, carbon, etc., can be used as current collectors. Generally, aluminum is used for the cathode and
5 copper is used for the anode.

The active materials are the most crucial component of electrochemical cells since they determine the performance of cells in view of the fact that the charge and discharge reaction (or
10 oxidation/reduction reaction) of cells take place on these materials. Furthermore, the active materials possess the largest content in the active material layer. As cathode active materials, it is possible to use oxide compounds or sulfide compounds of transition metals, organic compounds, polymer compounds, etc. Preferably, it is possible to use
15 oxide compounds or polymer materials such as lithium cobalt oxide (Li_xCoO_2), lithium nickel oxide (Li_xNiO_2), lithium nickel cobalt oxide ($\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$), spinel type lithium manganese oxide ($\text{Li}_x\text{Mn}_2\text{O}_4$), manganese dioxide (MnO_2), etc. As anode active materials, alkali metals, alkali earth metals, carbon, oxide compounds or sulfide
20 compounds of transition metals, organic compounds and polymer compounds may be used, preferably carbon or polymer materials can be used. It is essential that the active materials should be chosen in accordance with the desired performance or use of cells.

25 The conducting materials refer to materials that are added to the cathode or anode in order to improve the electronic conductivity, and are generally carbon. Among them, conducting materials are preferably

graphite, cokes, activated carbon and carbon black, more preferably graphite and carbon black. One or two or more of conducting materials selected from the above group can be used and there is no difference whether they are synthetic or natural materials. The conducting materials are added in an amount of 3 to 15 % by weight based on the total weight of the electrode materials. If the amount of the conducting materials added is not more than 3 % by weight, the electrical conductivity falls, causing the problem of over voltage. If the amount exceeds 15% by weight, the energy density per unit volume decreases and the side reaction due to the conducting materials become severe.

The binders refer to components to be added to enhance the binding ability of the active materials and are generally polymer compounds. The polymer compounds that are used in the preparation of the solid electrolyte film may serve as binders. It is preferable to use binders, which are the same as polymers of the electrolyte film or have miscibility. The binders may be added in an amount of 15 % by weight or less based on the total weight of the electrode materials. If the amount of binders is less than required, the binding ability of the electrodes may decrease. If the amount of binders exceeds 15 % by weight, the processability and porosity of the electrodes decrease.

The additives refer to materials, which are added to improve the performance of cells or electrodes and can be chosen within a wide range in accordance with desired performances or use. The additives are added to improve the binding ability with composite electrodes inside or current collectors, to induce the porosity or non-crystallinity

of the composite electrodes, to improve the dispersibility of the composite electrode constituting materials or the efficiency of the process for the manufacturing of the electrodes, to prohibit the overcharge/overdischarge of the active materials, to recombine or
 5 remove the side reaction products, or to improve the absorption ability of the liquid electrolytes. Generally, salts, organic/inorganic compounds, minerals and polymer compounds can be used as additives, and absorbents added to the electrolyte film can be chosen.

10 In the following, the rechargeable lithium cell according to the present invention will be explained in greater detail.

The porous electrolyte film in a dried solid condition obtained by the above-mentioned process without having the step introducing the
 15 liquid electrolyte is assembled with a cathode and an anode prepared separately to form a cell, to which a liquid electrolyte is absorbed to obtain the rechargeable lithium cell. The solid electrolyte should be subjected to an activation step absorbing the liquid electrolyte in order to have a sufficient ionic conductivity for being used. By passing
 20 through the activation step, the solid electrolyte comes to be workable as an electrochemical cell. In case that the solid electrolyte fails to pass through the activation step, the ionic conductivity at room temperature decreases drastically, which renders the solid electrolyte itself inappropriate as an electrolyte.

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The process for the preparation of the cathode and/or anode to be assembled with said electrolyte film is as follows. Each mixture of the

cathode or anode materials is kneaded to give slurry. The resulting slurry is made to a thin film by means of casting, coating and screen printing and then the resulting thin film is combined with a current collector by means of pressing or lamination to form a cathode and/or
5 an anode. Alternatively, the slurry may be directly coated on a current collector to form a cathode and/or an anode.

Onto the surface of the electrodes manufactured by the above mentioned methods a solid electrolyte slurry consisting of an absorbent,
10 a polymer binder and a solvent may be directly applied to form a cell in which an electrolyte film is formed on the electrodes. Alternatively, one may constitute a cell by lamination or pressing the separately manufactured electrodes and electrolyte film. When a cell is constructed by the former method, the binding ability between the
15 electrodes and the electrolyte film may increase. However, it will be hard to adopt the former method when the electrodes and the electrolyte film do not correspond with each other, or when the electrodes or the electrolyte film are easy to pollute or lose their performance in the course of manufacturing process. Moreover, in case
20 that the electrolyte film is prepared by the dry process, electrodes may be contaminated by the non-solvents or pore formers which are used to introduce porous structures, which is problematic. Particularly, when water is used as a non-solvent or a pore former, the cell performance may be deteriorated if water is not completely removed by sufficient
25 drying step. In addition, there is a problem in that it is very hard to approach the complete drying condition. In the latter method, although there is a demerit in that the binding ability between the electrodes and

the electrolyte film is weak, there are much better merits in that it simplifies the quality control, process design and equipment used. Therefore, the latter method is preferred to the former one.

5 The electrolyte film prepared by the present invention contains an absorbent and thus has advantages in that it has higher mechanical strength as compared to pure electrolyte films or other electrolyte films containing gel type polymer electrolytes or plasticizers. Accordingly, because the electrolyte film of the present invention shows little change
10 in its shape during the pressing or lamination procedure and has high reproducibility, it has merits in that it can be produced with a low failure rate and on a large scale. Namely, it can be stated that the electrolyte film prepared by the present invention has properties suitable for pressing or lamination methods, which are more
15 advantageous in terms of quality control, process design and equipment used.

Brief Description of Drawings

20 Figure 1 is a cross sectional view of the cell wherein the solid electrolyte according to the present invention is used.

Figure 2 shows graphs demonstrating the experimental results of linear sweep voltammetry to determine the electrochemical stability of
25 the solid electrolyte according to the present invention.

Figure 3 shows a variation of discharge capacity of the cell in which the solid electrolyte containing an inorganic absorbent is used as compared to the cell in which polymer absorbent is used with repeated charge and discharge.

5

Drawing Reference Numerals:

1: solid electrolyte	11: absorbent powder
2: cathode	22: cathode current collector
3: anode	33: anode current collector

10

Best Mode for Carrying out the Invention

In the present invention, the solid electrolyte according to the present invention and the process for the preparation of cells by using said solid electrolyte is explained in detail. Firstly, the production of the solid electrolyte and the examination of performances were carried out. In addition, the solid electrolyte is assembled together with the anode and cathode to form a cell and then the procedure to examine the performance of the cell is described. However, the present invention is not restricted to those examples and various modifications are possible within the scope of the invention.

Example 1 (wet process)

An absorbent and PVdF powder were introduced to a 20 *ml* vial and then dry mixed for approximately 5 minutes with a magnetic stirrer. To the resulting mixture 4 *ml* of N-methyl pyrrolidinone was added and then continuously stirred until the binder was completely dissolved. In

order to prohibit the absorbent particles from agglomerating with each other, the resulting solution was further subjected to ultrasonic stirring for 30 minutes while stirring. The mixed solution thus prepared was coated onto a glass plate in thickness of 100 μm . The coated film was soaked in a non-solvent bath for approximately 10 minutes, which was removed from the bath and then dried at 40°C for 1 hour. The porous electrolyte film thus prepared was soaked in a liquid electrolyte solution for approximately 10 minutes. After the liquid electrolyte was completely absorbed, the weight change was determined. The ionic conductivity was also determined by the use of an alternate current impedance method.

Table 1 summarizes the kinds of absorbents and binders, the properties of the porous solid electrolyte in accordance with its content and conductivity. In order to compare the ability of the porous electrolyte film absorbing the liquid electrolyte, sorption capacity (Δ_{ab}) was defined as follows:

$$\Delta_{\text{ab}} = [\text{amount of the liquid electrolyte absorbed (mg)}]/[\text{weight of the electrolyte film (mg)}]$$

Table 1

E x.	Absorbents		PV dF	non- solvent	Liquid Electrolyte	Δ_{ab}	Ionic Conducti vity mS/cm	Mechani cal strength
	Kind	g	g					
a	Paragonite	0.13	0.28	H ₂ O	EC/DMC 1M LiPF ₆	7.0	2.1	Good

b	Paragonite	0.17	0.26	H ₂ O	EC/DMC 1M LiPF ₆	6.8	2.2	Good
c	Paragonite	0.72	0.24	H ₂ O	EC/PC 1M LiPF ₆	6.9	1.9	Good
d	Paragonite	1.06	0.26	H ₂ O	EC/PC 1M LiPF ₆	7.5	1.8	Good
e	Paragonite	1.51	0.26	H ₂ O	EC/DMC 1M LiPF ₆	8.0	2.4	Good
f	Paragonite	2.00	0.26	H ₂ O	EC/DMC 1M LiPF ₆	8.5	2.5	Good
g	Paragonite	1.98	0.25	Ethanol	EC/DMC 1M LiPF ₆	5.1	1.0	Good
h	Zeolite	1.37	0.60	H ₂ O	EC/DMC 1M LiPF ₆	7.2	1.9	Good
i	Zeolite	1.50	0.38	H ₂ O	EC/DMC 1M LiPF ₆	8.2	2.0	Good
j	Zeolite	1.65	0.29	H ₂ O	EC/DMC 1M LiPF ₆	8.0	2.4	Good
k	Montmoril lonite	1.34	0.58	H ₂ O	EC/DMC 1M LiPF ₆	8.0	2.8	Good
l	Montmoril lonite	1.50	0.38	H ₂ O	EC/DMC 1M LiPF ₆	8.2	2.9	Good
m	Porous Silica	1.35	0.59	H ₂ O	EC/DMC 1M LiPF ₆	8.5	2.4	Good
n	Polypropyl ene	1.35	0.60	H ₂ O	EC/DMC 1M LiPF ₆	7.0	1.9	Good
o	Wood powder	1.35	0.60	H ₂ O	EC/DMC 1M LiPF ₆	7.4	2.0	Good

Example 2 (wet process)

5 Paragonite powder and a binder powder were introduced to a 20 *ml* vial and then dry mixed for approximately 5 minutes with a magnetic stirrer. To the resulting mixture 4 *ml* of N-methyl pyrrolidinone was added and then continuously stirred until the binder was completely dissolved. In order to prohibit the absorbent particles

10 from agglomerating with each other, the resulting solution was further subjected to ultrasonic stirring for 30 minutes while stirring. The mixed solution thus prepared was coated onto a glass plate in thickness of 100 μm . The coated film was soaked in a water bath for 10 minutes, which was removed from the bath and then dried at 40°C for

15 approximately one hour. The porous electrolyte film thus prepared was

soaked in a liquid electrolyte solution for approximately 10 minutes. After the liquid electrolyte was completely absorbed, the weight change was determined. The ionic conductivity was also determined by the use of an alternate current impedance method. The results are summarized in Table 2.

Table 2

E x.	Paragonite	Binder		Liquid Electrolyte	Δ_{ab}	Ionic Conducti vity mS/cm	Mechani cal strength
	g	Kind	g				
a	1.98	PVdF	0.24	EC/DMC 1M LiPF ₆	8.1	2.4	Good
b	2.00	P(VdF-HFP)	0.26	EC/DMC 1M LiPF ₆	8.0	2.6	Good
c	1.95	PAN	0.25	EC/DMC 1M LiPF ₆	7.8	2.2	Good
d	2.00	PU	0.26	EC/DMC 1M LiPF ₆	8.9	2.9	Good
e	1.98	PVC	0.25	EC/DMC 1M LiPF ₆	7.4	2.0	Good
f	2.00	P(VdF-HFP)	0.26	EC/DMC 1M LiPF ₆	8.5	2.5	Good

Example 3 (dry process)

1.17 g of paragonite and 0.5 g of P(VdF-HFP) were introduced to a 20 ml vial and then dry mixed for approximately 5 minutes with a magnetic stirrer. To the resulting mixture 8 g of acetone was added and then continuously stirred until the binder was completely dissolved. In order to prohibit the absorbent particles from agglomerating with each other, the resulting solution was further subjected to ultrasonic stirring for 30 minutes while stirring. To the resulting mixed solution 0.9 g of ethylene glycol, 0.1 g of Triton X-100 and 1.8 g of isopropanol were added and then the resulting mixture was subjected to ultrasonic

stirring for approximately 10 minutes until the added mixture was uniformly mixed. The mixed solution thus prepared was coated onto a glass plate in thickness of 100 μm . The coated film was dried at 40°C for approximately 2 hours, which was further dried for approximately 6 hours in a vacuum drier set to 50°C. The electrolyte film thus prepared was soaked in an EC/DEC 1M LiPF_6 solution for approximately 10 minutes. After the liquid electrolyte was completely absorbed, the weight change was determined. Δ_{ab} value measured by the use of the weight change was 7.5. The conductivity determined at room temperature by an alternate current impedance method was 2.0×10^{-3} S/cm.

Example 4 (Comparative Example)

2 g of paragonite and 0.26 g of PVdF were introduced to a 20 *ml* vial and then dry mixed for approximately 5 minutes with a magnetic stirrer. To the resulting mixture 4 *ml* of N-methyl pyrrolidinone was added and then continuously stirred until the binder was completely dissolved. In order to prohibit the absorbent particles from agglomerating with each other, the resulting solution was further subjected to ultrasonic stirring for 30 minutes while stirring. The mixed solution thus prepared was coated onto a glass plate in thickness of 100 μm . The coated film was dried at room temperature for approximately 2 hours and then was further dried for 6 hours in a vacuum drier. The temperature of the vacuum drier was controlled to approximately 50°C. The present example differs from Examples 1 to 3 in the fact that a process for forming porous structures was not

conducted. The electrolyte film thus prepared was soaked in a liquid electrolyte solution for approximately 10 minutes. After the liquid electrolyte was completely absorbed, the weight change was determined. The conductivity was determined by the use of an alternate
5 current impedance method. Lithium ionic conductivity measured at room temperature was 7.0×10^{-4} S/cm.

Example 5

10 In order to determine the electrochemical stability of the porous solid electrolyte, the linear sweep voltammetry method was carried out by the use of a stainless steel (#304) as an operating electrode and lithium metal as an opposite electrode and a standard electrode. The electrochemical voltage applied in the linear sweep voltammetry was
15 from an open circuit voltage to 5.5V. The scan rate of the linear sweep voltammetry was 10mV/sec. The results of the linear sweep voltammetry measured on the porous solid electrolyte prepared by the methods of Example 1-(f), 1-(j), 1-(l) and 2-(s) are shown as A, B, C and D, respectively, in Fig. 2.

20

Example 6

In order to determine the performances of the cell using the solid electrolyte, an oxide compound cathode, a carbon anode and a solid
25 electrolyte according to the present invention were assembled to fabricate cells, and then the charge and discharge test on thus fabricated cells was carried out. The fabricated cells were in a laminated form and

Table 3

Ex.	Cathode				Anode				Solid Electrolyte	Fig.
	Active material	Conducting material	Binder	Additive	Active material	Conducting material	Binder	additive		
v	LiCoO ₂	Carbon black	PVdF	Paragonite	Graphite	Carbon black	PVdF	Paragonite	Ex. 1-(e)	Fig.3-E
w	LiCoO ₂	Carbon black	PVdF	Zeolite	Graphite	Carbon black	PVdF	Zeolite	Ex.1-(j)	Fig.3-F
x	LiCoO ₂	Carbon black	PVdF	Zeolite	Graphite	Carbon black	PVdF	Zeolite	Ex.1-(n)	Fig.3-G
y	LiCoO ₂	Carbon black	P(VdF-HFP)	Zeolite	Graphite	Carbon black	P(VdF-HFP)	Zeolite	Ex.3	Fig.3-H
z	LiMn ₂ O ₄	Carbon black	P(VdF-HFP)	Paragonite	Graphite	Carbon black	P(VdF-HFP)	Paragonite	Ex.2-(q)	Fig.3-I

Fig.3 illustrates the discharge capacity with repeated charge and discharge of the cell obtained by the respective examples in comparison with the first discharge capacity. From the test results, it was confirmed that the use of the solid electrolytes containing inorganic absorbents (Examples 6-v, w, z) shows much better cell performances than that of the solid electrolyte containing organic absorbents such as polymers (Example 6-x). Furthermore, it was also confirmed that the use of solid electrolytes obtained by the wet process according to the present invention (Examples 1 and 2) shows much better cell performances than that of the solid electrolyte obtained by the dry process (Example 6-y). Namely, the solid electrolyte containing inorganic absorbent and prepared by the wet process has a much better effect on the total cell performances (charge and discharge performance, etc.), although the electrolyte film or solid electrolyte itself does not show any significant differences in properties (ionic conductivity, mechanical strength, etc.).

Industrial Applicability

The microporous solid electrolytes according to the present invention are characterized by the following facts:

they have high mechanical strength, which makes them suitable to be made into thin films;

they have high ionic conductivity corresponding to that of the liquid electrolytes since the microporous structures and absorbents

introduced to the polymer matrix facilitate the absorption of the liquid electrolyte and there is no restriction on the transfer of lithium ions;

unlike general polymer electrolytes in gel type, they do not require any particular dehumidifying atmosphere since lithium salt, which is easily decomposed by a trace amount of moisture, is not introduced during the manufacturing of the electrolyte films;

they have a broad electrochemical potential window since the absorbent therein is electrochemically stable; and

they are of ease in automation for mass production due to the simple process for the production of the electrolyte.

In addition, it is possible for the microporous solid electrolyte according to the present invention to minimize the surface resistance between the electrolyte and electrodes since the binding ability with the cathode and anode is excellent and the volume change due to the introduction of the liquid electrolyte is little. Therefore, the microporous solid electrolyte according to the present invention is suitable for being used as an electrolyte for rechargeable lithium cells. The solid electrolytes containing inorganic absorbents also show superior mechanical, thermal and electrochemical stability to those of the solid electrolytes containing organic absorbents, thereby showing less decrease in their discharge capacity during the repeated charge and discharge. When introducing porous structures to the electrolyte, the wet process is more efficient and stable than the dry process. The microporous solid electrolyte shows superior performances such as less decrease in their discharge capacity as mentioned above when they are used to form electrochemical cells.